Non-universality of commonly used correlation-energy density functionals

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Abstract

The correlation energies of the helium isoelectronic sequence and of Hooke's atom isoelectronic sequence have been evaluated using an assortment of local, gradient and meta-gradient density functionals. The results are compared with the exact correlation energies, showing that while several of the more recent density functionals reproduce the exact correlation energies of the helium isoelectronic sequence rather closely, none is satisfactory for Hooke's atom isoelectronic sequence. It is argued that the uniformly acceptable results for the helium sequence can be explained through simple scaling arguments that do not hold for Hooke's atom sequence, so that the latter system provides a more sensitive testing ground for approximate density functionals. This state of affairs calls for further effort towards formulating correlation-energy density functionals that would be truly universal at least for spherically-symmetric two-fermion systems.

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1 Introduction

Density functional theory (dft) can be implemented in a variety of ways, all of which have their roots in the pre-Hohenberg-Kohn era. A fully consistent implementation requires the formulation of density functionals for the kinetic energy as well as for the exchange and correlation energies, none of which can be expressed in terms of the one-particle density in a straightforward way. The Kohn-Sham formulation depends on the construction of a local one-body potential that incorporates the effect of interelectronic repulsion, giving rise to a ground state density that coincides with that derived from the solution of the exact many-body hamiltonian. Finally, an approximate approach, based on the fact that the Hartree-Fock density is fairly close to the exact one, proposes that the exact ground state energy be evaluated by adding to the Hartree-Fock energy a correlation energy, calculated in terms of the Hartree-Fock density by means of an appropriate density functional.

Since the ultimate correlation-energy density functional, whose existence is guaranteed by the Hohenberg-Kohn theorem, remains elusive, the development and testing of ever improved density functionals keeps being vigorously pursued. For an extensive recent study see Kurth, Perdew and Blaha [1]. In this vein, Chakravorty *et al.* [2] and Jarzecki and Davidson [3] compared the exact and dft correlation energies across the helium (and other) atomic isoelectronic sequences. In the former article the exact correlation energy for the ground state of the helium isoelectronic sequence (as well as for all other atomic isoelectronic sequences with up to 18 electrons) is compared with the values obtained using six density functionals (i.e., LYP [4], CS [5], VWN-SPP [6], PZ [7], B88 [8], LC [9] — the acronyms will be explained below). Of these, only the LYP correlation energies are uniformly close to the exact values over the range of nuclear charges examined. B88 grows to become twice as large as the exact correlation energy, and all the others seem to diverge for large Z. The latter article extends this study, considering P86 [10], LYP [4] (again), and PW91 [11] as well as various combinations of these with exchange functionals. While, as noted above, the correlation energy obtained with the LYP functional (evaluated for the Hartree-Fock density) follows the exact correlation energy rather closely, this is not the case if the same functional is combined with

Becke's exchange functional. On the other hand, the combination BP86 (Becke's exchange with the P86 correlation functional) exhibits a rather close agreement with the exact correlation energies for the helium isoelectronic sequence. The overall conclusion of these authors is "all DFT functionals, [...] reveal problems in descriptions of the energy as a function of nuclear charge" [3]. Correlation energies were also evaluated by Umrigar and Gonze [12] for several members of the helium isoelectronic sequence, in terms of both local and GGA-type density functionals.

The high Z limit of the helium (and other) isoelectronic sequences within dft was carefully examined by Whittingham and Burke [13], who pointed out that some correlation-energy functionals do not scale correctly to the high-density limit. In particular, the local-density approximation diverges logarithmically at large Z, and the Perdew-Wang (PW91) functional [11] fails as well. They note that PBE [14] was designed to correct for this failure.

The over-estimate of atomic correlation energies by local density approximations based on the homogeneous electron gas has been analyzed by Tong [15], who attributed it to the continuous excitation spectrum of the latter, infinitely extending, system, that allows for a "soft" response to the internuclear repulsion. A modification of the local density approximation, in which an energy gap is introduced, was recently studied by Rey and Savin [16]. Their results suggest that the inhomogeneity needs to be introduced more explicitly.

An analysis of the properties that correlation-energy density functionals should satisfy in order to present a valid behavior along isoelectronic sequences was presented by Staroverov *et al.* [17], who, as Whittingham and Burke [13], studied the high Z limit of some two-electron atomic ions. Furthermore, an interesting methodological discussion of the construction of density functionals was recently presented by Perdew *et al.* [18]. These authors make a strong case for nonempirical functionals and specifically recommend the PBE [14] and the TPSS [19] functionals.

Hooke's atom consists of two "electrons" that repel one another like ordinary electrons but are bound to the "nucleus" via harmonic potentials. Its separability, in center-of-mass and relative coordinates, was pointed out by Kestner and Sinanoglu [20], and the fact that

for certain values of the force constant it is analytically solvable was noted by Kais *et al.* [21] and, more systematically, by Taut [22]. Several studies for Hooke's atom have been performed, aimed at deriving exact density functionals or Kohn-Sham type exchange-correlation potentials [23-25], most notably by Burke *et al.* [26-30] and Ludena *et al.* [31]. However, a systematic study over a broad range of force constants has not been presented, to the best of our knowledge, with the exception of the local-density calculations that were carried out by Huang and Umrigar [32].

In the present paper we examine an assortment of correlation-energy density functionals proposed over the last seventy(!) years. Virtually each one of them had been tested for the helium atom, and most of them had been tested for a range of atomic ions isoelectronic with helium. Needless to say, many of them have been applied, with varying degrees of success, to the study of heavier atoms as well as molecules, surfaces and solids, and share the credit for the immense impact of dft in all these areas.

The Hohenberg-Kohn theorem implies that the ground-state correlation energy is a universal functional of the ground state density. The examination of the extent to which the commonly used correlation-energy density functionals satisfy this property is the principal aim of the present paper. This is carried out by considering the performance of the presently selected set of correlation energy density functionals for Hooke's atom isoelectronic sequence. Since these density functionals were originally developed for Coulombic (atomic and molecular) systems, their performance for Hooke's atom provides a severe test of their universal validity. Moreover, Hooke's atom remains bound over the whole range, $0 < k < \infty$, of the force constant. This fact allows correlation to be examined not only in the high k (weak correlation) limit but also in the low k (strong correlation) limit. The latter limit is not available for atomic systems, that become unbound below a certain critical nuclear charge. This property of Hooke's atom isoelectronic sequence is elaborated upon below.

Another model system with similar properties is that of a two interacting particles confined to a spherical volume. Here, the radius of the sphere provides a parameter that, upon variation, can be used to change the system from the low correlation to the strong correla-

tion limit. This system was recently studied in detail by Jung *et al.* [33] who also compared the exact exchange and correlation energies with those obtained by some few approximate functionals. Thus, the combined results of their and our study provide detailed insight into the accuracies of currently applied approximate density functionals and, consequently, may be used in improving those.

Ultimately, the physical reason behind the existence of correlation effects is the electron-electron interactions. Thus, the total correlation energy can be written in terms of a double-integral over two position coordinates, involving the exact and the Hartree-Fock first and second order reduced density matrices,

$$E_c = \int \int \rho(\vec{r}_1)\rho(\vec{r}_2)\tilde{\epsilon}_c(\vec{r}_1, \vec{r}_2)d^3\vec{r}_1 d^3\vec{r}_2, \tag{1}$$

where $\tilde{\epsilon}_c(\vec{r}_1, \vec{r}_2)$ is a unique correlation-energy density in a six-dimensional $(\vec{r}_1, \vec{r}_2)$ space. On the other hand, in density functional theory it is common practice to write the correlation energy as

$$E_c = \int \rho(\vec{r})\epsilon_c(\vec{r})d^3\vec{r}. \tag{2}$$

The transformation from Eq. (1) to Eq. (2) is not unique. Therefore, different approximate expressions for $\epsilon_c(\vec{r})$ may look very different but nevertheless give very close total correlation energies E_c [34]. Thus, since the approximate correlation-energy functionals most often are given in terms of approximate forms for $\epsilon_c(\vec{r})$, it is not possible to compare those directly and thereby obtain information on their performance.

Instead, only the total correlation energy is of physical relevance. Therefore, by considering the total correlation energy for continuous classes of systems detailed information on the performance of approximate density functionals can be obtained, that ultimately can be used in assessing their performance as well as in improving them. The helium isoelectronic sequence provides such a class of systems, as also is the case for Hooke's atom sequence. However, as briefly pointed out above and as we shall demonstrate more carefully below, the former sequence is less general than what initially may be assumed, making it less informative for studies of approximate energy functionals. On the other hand, as we shall

also demonstrate, Hooke's atoms provide a class of systems for which the members are "less similar" than is the case for the helium sequence, making a detailed study of this sequence highly relevant.

We finally add that correlation energy is defined differently in wave function methods and in density functional theory. Since the numerical differences are not large and not will affect any of the conclusions of the present work, we shall not discuss this distinction further.

2 The spherical two-electron systems

The ground state of a spherically symmetric two particle system with the Hamiltonian

$$\mathcal{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + v(r_1) + v(r_2) + \frac{1}{r_{12}}\,, \tag{3}$$

in which the (local) single-particle potential $v(r)$ is sufficiently attractive, is a bound singlet; hence, it satisfies $\rho_\alpha = \rho_\beta$, where ρ_α and ρ_β are the spin up and spin down densities, respectively; i.e., the spin polarization parameter $\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta}$ vanishes. The spatial part of the corresponding Hartree-Fock wavefunction is of the form $\Phi_{HF}(\vec{r_1}, \vec{r_2}) = \phi(r_1)\phi(r_2)$, and the electron density is given in the form $\rho(r) = 2\phi(r)^2$. It will be useful to note that $|\nabla\rho(r)| = \frac{d\rho}{dr}$, $\left(\frac{d\phi}{dr}\right)^2 = \frac{1}{8\rho}\left(\frac{d\rho}{dr}\right)^2$, and $\nabla^2\rho = \frac{d^2\rho}{dr^2} + \frac{2}{r}\frac{d\rho}{dr}$. Moreover, in the present context $\left(\frac{d\phi}{dr}\right)^2 = \frac{1}{8\rho}\left(\frac{d\rho}{dr}\right)^2$. For each of the density functionals considered below we provide the (sometimes considerably simplified) expression appropriate for the family of spherically symmetric two-particle systems presently studied. One reason for doing so is that the expressions for the various density functionals are scattered in the literature, in many instances the expression for a particular functional requiring consultation of several different sources whose notation is occasionally not fully consistent. The record is held by TPSS, the specification of which requires consultation of ref. [19], [35], [14], and [11].

In our case we have

$$v(r) = \begin{cases} \frac{-Z}{r} & \text{for the helium sequence} \\ \frac{1}{2}kr^2 & \text{for Hooke's atom.} \end{cases} \tag{4}$$

The correlation energy is given in terms of an expression of the form

$$E_c = \int_0^\infty 4\pi r^2 \rho(r) \epsilon_c[\rho] dr$$

where $\epsilon_c[\rho]$ is a correlation energy density whose value at r may depend on the values of ρ, $\frac{d\rho}{dr}$ as well as $\frac{d^2\rho}{dr^2}$ at r. The dependence of the various functionals on the density is usually expressed via the Wigner-Seitz radius (the radius of a sphere containing one particle with uniform density ρ)

$$r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3} .$$

We follow the classification of $\epsilon_c[\rho]$ into

- Zero-order approximation (0OA), depending on ρ only,
- First-order approximation (1OA), depending on $\frac{d\rho}{dr}$ as well,
- Second-order approximation (2OA), depending also on $\frac{d^2\rho}{dr^2}$.

We note that this classification is closely related to the common classification into local density approximations (LDAs), generalized-gradient approximations (GGAs) and meta-GGAs. However, by restricting the classification according to the behavior for a spherical two-electron system, for a given functional we sometimes arrive at an expression that belongs to a lower class, in the classification specified above, than the general case. Our classification here applies to this reduced expression.

Both as an additional check of the computations and to gain further insight into the behavior of the various density functionals considered, we examine the weak correlation limit ($Z \to \infty$ or $k \to \infty$, for the Helium and Hooke's atom isoelectronic sequences, respectively) of the corresponding correlation energies. This can be done by using the asymptotic densities

$$\rho(\mathrm{He}) = \frac{2Z^3}{\pi} \exp(-2Zr), \quad Z \to \infty$$

and

$$\rho(\mathrm{Hooke}) = 2\left(\frac{\omega}{\pi}\right)^{3/2} \exp(-\omega r^2), \;\; \omega = \sqrt{k}, \quad k \to \infty \, .$$

In fact, the density, correct to first order in the interelectronic repulsion, can be written for the Helium isoelectronic sequence by replacing the nuclear charge Z by the screened nuclear charge $Z_{\rm eff} = Z - 5/16$. Similarly, for Hooke's atom the variational principle yields for the trial function $\left(\frac{\omega_{\rm eff}}{\pi}\right)^{3/4} \exp(-\frac{\omega_{\rm eff}}{2} r^2)$ the equation $\omega_{\rm eff}^2 + \frac{1}{3}\sqrt{\frac{2}{\pi}}\omega_{\rm eff}^{3/2} - \omega^2 = 0$, where $\omega = \sqrt{k}$. The solution, to first order, can be written in the form $\omega_{\rm eff} \approx \left(\sqrt{\omega} - \frac{1}{12}\sqrt{\frac{2}{\pi}}\right)^2$. In fact, to study the weak correlation limit it is convenient to use the scaled radial coordinate $\tilde{r} = Z_{\rm eff} r$ or $\tilde{r} = \omega_{\rm eff}^{1/2} r$, for the Helium and Hooke's atom isoelectronic sequences, respectively. In terms of these coordinates $\rho(r) 4\pi r^2 dr$ becomes $8 \exp(-2\tilde{r}) \tilde{r}^2 d\tilde{r}$ or $\frac{8}{\sqrt{\pi}} \exp(-\tilde{r}^2) \tilde{r}^2 d\tilde{r}$, respectively. In terms of these scaled coordinates the expressions $\frac{d\rho}{dr}\rho^{-4/3}$, $\frac{1}{r}\frac{d\rho}{dr}\rho^{-5/3}$ and $\frac{d^2\rho}{dr^2}\rho^{-5/3}$, that appear in several of the GGA and meta-GGA density functionals, obtain Z- (or k-) independent forms in the weak correlation limit. The weak correlation limit for the various density functionals examined below should be compared with the exact values [36]

$$E_c({\rm He}) \approx -0.046663 + \frac{0.009739}{Z}$$

and

$$E_c({\rm Hooke}) \approx -0.049703 + \frac{0.009369}{k^{1/4}} \, .$$

3 Zero order approximations

3.1 Wigner's functional

Wigner's first exploration of the correlation energy density as a means for estimating correlation energies in many-electron systems dates back to 1934 [37]. Four years later he proposed the functional [38]

$$\epsilon_c^W(r_s) = -\frac{0.44}{7.8 + r_s} \, . \tag{5}$$

In the weak-correlation limit (i.e., when either $Z \to \infty$ or $k \to \infty$) Wigner's correlation energy for a two-electron system becomes $-\frac{2 \cdot 0.44}{7.8} = -0.113$, which is roughly twice as large as the corresponding (rather similar) limiting values of the helium and Hooke's atom isoelectronic sequences. A closer examination yields $E_c^W({\rm He}) \approx -0.113 + \frac{0.035}{Z}$ and

$E_c^W(\text{Hooke}) \approx -0.113 + \frac{0.023}{k^{1/4}}$. These expressions are easily obtained analytically, noting that in this limit $\epsilon_c^W \approx -\frac{0.44}{7.8} + \frac{0.44}{7.8^2} r_s$. In the strong correlation limit $\epsilon_c^W \approx -\frac{0.44}{r_s}$.

3.2 The Gunnarsson-Lundqvist functional [39]

$$\epsilon_c^{GL} = -0.0333 \left[(1 + x_p^3) \log(1 + \frac{1}{x_p}) + \frac{x_p}{2} - x_p^2 - \frac{1}{3} \right] \tag{6}$$

where $x_p = \frac{r_s}{11.4}$. Since for $r_s \to 0$ one has $\epsilon_c^{GL} \approx 0.0333 \log(r_s)$, it follows, using the asymptotic densities specified above, that

$$E_c^{GL}(\text{He}, Z \to \infty) \approx -2 \cdot 0.0333 \log(Z) - 0.09506\,,$$

and

$$E_c^{GL}(\text{Hooke}, k \to \infty) \approx -\frac{0.0333}{2} \log(k) - 0.116\,.$$

The leading asymptotic terms for the helium and Hooke's sequences are related to one another by the substitution of $k^{\frac{1}{4}}$ for Z, which is consistent with McWeeny's correspondence [40]. In the low density (strong correlation) limit, $r_s \to \infty$, hence $\epsilon_c^{GL} \approx -\frac{0.285}{r_s}$.

3.3 The Brual-Rothstein functional [41]

This correlation energy density

$$\epsilon_c^{BR} = -\frac{1}{9.81 + 21.437\rho^{-1/3}} = -\frac{0.0289}{0.284 + r_s} \tag{7}$$

has the same form as Wigner's functional, eq. 5. The parameterization has been chosen to yield an exact correlation energy for the helium atom.

Just like Wigner's functional, the weak correlation limit yields a common correlation energy for the hydrogenic and Hooke's sequences, $E_c^{BR} = -0.204$.

3.4 The Perdew-Wang parameterization [11]

This is the up-to-date local density approximation, that we write in the form

$$\epsilon_c^{unif}(r_s) = -2c_0(1 + \alpha_1 r_s) \log\left[1 + \frac{1}{\tilde{\beta}_1 r_s^{1/2} + \tilde{\beta}_2 r_s + \tilde{\beta}_3 r_s^{3/2} + \tilde{\beta}_4 r_s^2} \right], \tag{8}$$

where

$$\begin{aligned} c_0 &= 0.031091 \\ \alpha_1 &= 0.21370 \\ \tilde{\beta}_1 &= 2c_0\beta_1 = 0.47232 \\ \tilde{\beta}_2 &= 2c_0\beta_2 = 0.22308 \\ \tilde{\beta}_3 &= 2c_0\beta_3 = 0.10187 \\ \tilde{\beta}_4 &= 2c_0\beta_4 = 0.030652\,. \end{aligned}$$

β_i, $i = 1, 2, 3, 4$, (along with c_0 and α_1) are given in [11]. In the weak correlation limit ($r_s \to 0$) one obtains $\epsilon_c^{unif}(r_s) \approx 2c_0 \log(\tilde{\beta}_1 r_s^{1/2})$, hence

$$E_c^{PW}(\text{He}) \approx -2c_0 \log(Z) - 0.05143\,,$$

and

$$E_c^{PW}(\text{Hooke}) \approx -\frac{c_0}{2}\log(k) - 0.07066\,.$$

These expressions agree with the computed correlation energies, presented in tables 1 and 4, respectively. In the strong correlation limit, $r_s \to \infty$, we obtain $\epsilon_c^{unif} \approx -\frac{0.434}{r_s}$, which is rather close to the corresponding limit of Wigner's correlation-energy density functional, eq. 5.

4 First-order approximations

4.1 The Perdew86 functional [10]

Define

$$A = 0.002568 + 0.023266 r_s + 7.389 \cdot 10^{-6} r_s^2$$

and

$$B = 1 + 8.723 r_s + 0.472 r_s^2 + 0.07389 r_s^3\,.$$

Then $C = 0.001667 + \frac{A}{B}$ and

$$\Phi = \frac{-0.0008129}{C} \cdot \frac{d\rho}{dr} \rho^{-7/6} \, .$$

The correlation energy density for the homogeneous electron gas is parameterized as follows [7]: For $r_s < 1$:

$$\epsilon_c^{(0)} = 0.0311 \log(r_s) - 0.048 + 0.0020 r_s \log(r_s) - 0.0116 r_s \, ,$$

$[E_c^{(0)}(\mathrm{He}, Z \to \infty) = -2 \cdot 0.0311 \log(Z);\ E_c^{(0)}(\mathrm{Hooke}, k \to \infty) = -\frac{0.0311}{2} \log(k)]$
and for $r_s > 1$:

$$\epsilon_c^{(0)} = \frac{-0.1423}{1 + 1.0529 r_s^{1/2} + 0.3334 r_s} \, .$$

[For $r_s \to \infty$, $\epsilon_c^{(0)} \approx -\frac{0.427}{r_s}$].

In terms of all the above, the correlation energy density is

$$\epsilon_c^{P86} = \epsilon_c^{(0)} + C \exp(-\Phi) \left(\frac{d\rho}{dr} \right)^2 \rho^{-7/3} \, .$$

In the $Z \to \infty$ (or $k \to \infty$) limit the non local term vanishes, because in this limit $\Phi \sim Z^{1/2}$ ($\Phi \sim k^{1/8}$, respectively) so $\exp(-\Phi) \to 0$.

4.2 Becke's functional [8]

Define $B = \left(\frac{d\rho}{dr} \right)^2 \rho^{-8/3}$. Then

$$E_x = -\rho^{1/3} \left(\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} + 0.00375 \cdot 2^{1/3} B \Big(1 + 0.007 \cdot 2^{2/3} B \Big)^{-4/5} \right) \, .$$

Now define $z = -\frac{0.63}{E_x}$. The expression for the correlation energy density is

$$\epsilon_c^{B88} = -0.2 \rho z^2 \left(1 - \frac{\log(1+z)}{z} \right) \, .$$

In the weak correlation limit it is found that $z \to 0$, hence $\epsilon_c^B \approx -0.1 \rho z^3$. Numerical integration over the asymptotic densities yields $E_c^{B88}(\mathrm{He}, Z \to \infty) = -0.07445$ and $E_c^{B88}(\mathrm{Hooke}, k \to \infty) = -0.22176$.

4.3 The Wilson-Levy functional [42]

This functional,

$$\epsilon_c^{WL} = \frac{-0.74860 + 0.06001 \left|\frac{d\rho}{dr}\right| \rho^{-4/3}}{3.60073 + 2.2679 \left|\frac{d\rho}{dr}\right| \rho^{-4/3} + r_s} \,, \tag{9}$$

is a non-local generalization of Wigner's functional. Numerical integration over the asymptotic densities yields $E_c^{WL}(\mathrm{He}, Z \to \infty) = -0.04803$ and $E_c^{WL}(\mathrm{Hooke}, k \to \infty) = -0.07817$.

4.4 The Perdew, Burke and Ernzerhof functional [14]

For a spherically symmetric singlet state this correlation-energy density is of the form

$$\epsilon_c^{PBE} = \epsilon_c^{unif}(r_s) + H(r_s, t) \,. \tag{10}$$

$\epsilon_c^{unif}(r_s)$ is given by eq. 8, and

$$H(r_s, t) = \gamma \log \left\{ 1 + \delta t^2 \left[\frac{1 + At^2}{1 + At^2 + (At^2)^2} \right] \right\} \,,$$

where $t = \frac{1}{4}\left(\frac{\pi}{3}\right)^{1/6} \rho^{-7/6} \frac{d\rho}{dr}$ and $A = \delta \left[\exp\left(-\frac{\epsilon_c^{unif}}{\gamma} \right) - 1 \right]^{-1}$. Here, $\gamma = c_0$ (*cf.* eq. 8) and $\delta = 2.1461$. The $Z \to \infty$ logarithmic leading term of $\epsilon_c^{unif}(r_s)$ is canceled by an equal term with opposite sign in $H(r_s, t)$. A recent comparative study [1] suggests that this correlation energy density functional is superior to all other density functionals considered in that study. The weak correlation limit requires numerical integration over the asymptotic densities, yielding $E_c^{PBE}(\mathrm{He}, Z \to \infty) = -0.04789$, in agreement with [14] and [17], and $E_c^{PBE}(\mathrm{Hooke}, k \to \infty) = -0.08131$.

4.5 The Filatov-Thiel density functional

Filatov and Thiel proposed two closely related functionals, that we shall designate FT97 (cf. [43, 44]) and FT98 (cf. [45]). Whereas FT97 belongs in the present subsection, FT98 contains a dependence on the Laplacian of the density and belongs in the following subsection.

FT97 "[...] is based on a model of the Coulomb hole distribution function and accurately describes the correlation energy of the uniform electron gas and the atoms He to Ar" [44]. Define

$$y_0 = \frac{1}{(18\pi)^{2/3}} \rho^{-8/3} \left(\frac{d\rho}{dr}\right)^2$$

and let

$$F_{97} = \frac{1 + 1.622199 y_0 + (0.489958 y_0)^2}{\sqrt{1 + 1.094530 y_0 / r_s}} \exp[-(0.489958 y_0)^2] \,. \tag{11}$$

Let

$$\mu = \frac{0.02940 r_s}{\left\{\left[1 + 0.370365 \exp(-0.10018 r_s^{4/5})\right] F_{97}\right\}^2} \,.$$

and

$$f(\mu) = -\exp(\mu) E_1(\mu) \,,$$

where $E_1(x)$ is the exponential integral.

The FT97 correlation density functional [43, 44] is

$$\epsilon_c^{FT97} = 0.015545 \left\{ f(\mu) + \frac{6 + 4\mu^{1/2} + 4\mu}{3 + 6\mu^{1/2} + 6\mu} [\mu f(\mu) + 1] \right\} \,. \tag{12}$$

In the weak correlation limit $E_c^{FT97}(\mathrm{He}) \approx -0.05648 + \frac{0.0198}{Z}$, and $E_c^{FT97}(\mathrm{Hooke}) \approx -0.07076 + \frac{0.07}{k^{1/4}}$.

4.6 The One-parameter progressive CS-type functional [46]

This correlation energy density is a variant of the Cole-Salvetti formula, discussed in subsection 5.1. Defining $x_\sigma = 2^{1/3} \rho^{-4/3} \frac{d\rho}{dr}$, this functional can be written in the form

$$\epsilon_c^{OP} = -0.38035 \, \rho \frac{\beta_{\alpha\beta} + 0.3789}{\beta_{\alpha\beta}^4 + 1.1284 \beta_{\alpha\beta}^3 + 0.3183 \beta_{\alpha\beta}^2} \tag{13}$$

where

$$\beta_{\alpha\beta} = 0.93934 \rho^{1/3} \left[3 \left(\frac{3}{4\pi}\right)^{1/3} + \frac{0.0084 x_\sigma^2}{1 + 0.0252 x_\sigma \log(x_\sigma + \sqrt{x_\sigma^2 + 1})} \right] \,.$$

In the weak correlation limit $E_c^{OP}(\mathrm{He}) \approx -0.08511 + \frac{0.085}{Z}$, and $E_c^{OP}(\mathrm{Hooke}) \approx -0.09504 + \frac{0.074}{k^{1/4}}$.

4.7 Perdew, Kurth, Zupan and Blaha functional [35]

This functional depends on the kinetic energy density, and is therefore a meta-GGA functional. However, for the ground state of the two-electron system it reduces to

$$\epsilon_c^{PKZB} = 1.53(\epsilon_c^{PBE} - \epsilon_c^{up}) \,, \tag{14}$$

where ϵ_c^{PBE} is given by eq. 10 and

$$\epsilon_c^{up} = \epsilon_c^{unif,up} + H^{up}(r_s, t) \,.$$

Here $\epsilon_c^{unif,up}$ has the same form as ϵ_c^{unif}, eq. 8, with the parameters c_0, α_1 and $\tilde{\beta}_i$, $i = 1, 2, 3, 4$ being replaced by

$$\begin{aligned}
\overline{c}_0 &= 0.015545 \\
\overline{\alpha}_1 &= \alpha_1 2^{1/3} = 0.25889 \\
\overline{\beta}_1 &= 2\overline{c}_0 \beta_1^{up} 2^{1/6} = 0.49273 \\
\overline{\beta}_2 &= 2\overline{c}_0 \beta_2^{up} 2^{1/3} = 0.24278 \\
\overline{\beta}_3 &= 2\overline{c}_0 \beta_3^{up} 2^{1/2} = 0.14801 \\
\overline{\beta}_4 &= 2\overline{c}_0 \beta_4^{up} 2^{2/3} = 0.03085 \,,
\end{aligned}$$

respectively. $\overline{c_0}$, α_1 and β_i^{up}, $i = 1, 2, 3, 4$ are presented in ref. [11], Table I. The fractional powers of 2 take care of the fact that the spin up density is a half of the total density, so r_s should otherwise have been replaced by $r_s 2^{1/3}$.

$H^{up}(r_s, t)$ is obtained from $H(r_s, t)$ by multiplying it by $\frac{1}{2}$, replacing A by

$$A^{up} = \delta \left[\exp\left(-\frac{2\epsilon_c^{unif,up}}{\gamma} \right) - 1 \right]^{-1} \,,$$

and replacing t by $t^{up} = t\sqrt{2}$.

Inspecting the reparametrized expression we note that

$$\epsilon_c^{unif,up}(r_s) \approx \frac{1}{2} \epsilon_c^{unif}(r_s) \,.$$

This is not apparent in terms of the parameterization given in [11].

Numerical integration over the asymptotic density functionals yields $E_c^{PKZB}(\mathrm{He}, Z \to \infty) = -0.05525$, in agreement with the value reported in the erratum to ref. [17], and $E_c^{PKZB}(\mathrm{Hooke}, k \to \infty) = -0.08468$.

4.8 The TPSS functional [19]

This functional is of the form

$$\epsilon_c^{TPSS} = \epsilon_c^{PKZB}(1 + 2.8\epsilon_c^{PKZB})$$

where ϵ_c^{PKZB} is given by eq. 14. The asymptotic correlation energies are $E_c^{TPSS}(\mathrm{He}, Z \to \infty) = -0.04901$, in agreement with the value reported in the erratum to ref. [17], and $E_c^{TPSS}(\mathrm{Hooke}, k \to \infty) = -0.06843$.

5 Second-order approximations

5.1 Colle-Salvetti formula

The Colle-Salvetti formula [5] for the correlation energy depends on the Hartree-Fock two-particle density matrix. For the ground state of a two-electron atom it can be written in terms of the Hartree-Fock density, providing a correlation energy density

$$\epsilon_c^{CS} = -0.04918 \, \frac{1 + 0.132\rho^{-5/3} \exp(-0.2533\rho^{-1/3}) \, \tau_{CS}}{1 + 0.349\rho^{-1/3}} \,, \tag{15}$$

where

$$\tau_{CS} = \frac{1}{8}\left[\frac{d^2\rho}{dr^2} + \frac{2}{r}\frac{d\rho}{dr} - \frac{1}{\rho}\left(\frac{d\rho}{dr}\right)^2\right] \,.$$

Integration over the asymptotic densities, which can be carried out analytically, yields $E_c^{CS}(\mathrm{He}, Z \to \infty) = -0.01941$ and $E_c^{CS}(\mathrm{Hooke}, k \to \infty) = -0.001772$, respectively.

5.2 Lee, Yang and Parr functional [4]

This correlation-energy density is obtained by replacing τ_{CS}, in eq. 15, by

$$\tau_{LYP} = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3} + \frac{7}{24}\left(\frac{d^2\rho}{dr^2} + \frac{2}{r}\frac{d\rho}{dr}\right) - \frac{17}{72\rho}\left(\frac{d\rho}{dr}\right)^2 .$$

For the $Z \to \infty$ (hydrogenic) density the LYP correlation energy functional can be integrated analytically, to yield the correlation energy -0.0566888. This value, obtained in ref. [17], appears to be too high (in absolute value) to be consistent with the values presented in Table 3. Closer examination reveals that the asymptotic behavior of the LYP correlation energy for the helium isoelectronic sequence is given by $E_c(\mathrm{He}) \approx -0.0566888 + 0.009\frac{\log^3(Z)}{Z}$. This expression, which is consistent with the numerical results, can be obtained analytically [48]. It is perhaps worth noting that using the screened hydrogenic density, in which Z is replaced by $Z - \frac{5}{16}$, the LYP functional yields, for $Z = 2$, the correlation energy -0.04388, compared to the value -0.04378 obtained with the Hartree-Fock density. For Hooke's atom isoelectronic sequence the asymptotic behavior of the correlation energy, at $k \to \infty$, is found to be $E_c(\mathrm{Hooke}) \approx -0.035501 + 0.00012\frac{\log^3(k)}{k^{1/4}}$.

5.3 FT98 [45]

This is a modified version of the FT97 functional, extended to include the Laplacian of the density. It can be written by replacing F_{97}, eq. 11, by

$$F_{98} = \frac{1 + (0.083726 y_\sigma)^2}{\sqrt{1 + 0.051581 y_\sigma / r_s}} \exp[-(0.083726 y_\sigma)^2] ,$$

where

$$y_\sigma = \frac{1}{(18\pi)^{2/3}}\rho^{-8/3}\left(\frac{d\rho}{dr}\right)^2 + \frac{0.89672}{(18\pi)^{4/3}}\rho^{-10/3}\left[\frac{1}{\rho}\left(\frac{d\rho}{dr}\right)^2 - \left(\frac{d^2\rho}{dr^2} + \frac{2}{r}\frac{d\rho}{dr}\right)\right]^2 .$$

In the weak correlation limit $E_c^{FT98}(\mathrm{He}) \approx -0.08173 + \frac{0.17}{Z}$, and $E_c^{FT98}(\mathrm{Hooke}) \approx -0.08706 + \frac{0.22}{k^{1/4}}$.

6 Performance of the various density functionals

The Hartree-Fock densities were evaluated for both the helium and Hooke's isoelectronic sequences, using the procedure described in ref. [49]. These densities were used to compute the correlation energies in terms of the various density functionals specified above. The results are presented in Tables 1-6, where comparisons with previous pertinent results are documented, as well as in Figures 1-8. When comparing the different results it is important to pay attention to the ranges of the correlation energy scales in the different Figures. Thus, Fig. 1, presenting the 0OA correlation energies for the helium isoelectronic sequence, has a range five times as large as Fig. 2 (crude 1OA), whose range is three times as large as that of Fig. 3 (better 1OA). The 2OA results, presented in Fig. 4, do not improve on the best 1OA results in Fig. 3. The overall trend is similar for Hooke's atom isoelectronic sequence, but much less pronounced. Thus, the range of Fig. 5 (0OA) is twice that of Fig. 6 (crude 1OA), where the range of deviations of the dft correlation energies from the exact values is only a factor of 1.5 broader than that in Fig. 7 (better 1OA). Again, the 2OA correlation energies do not improve on the best 1OA results.

The four 0OA functionals presented in Fig. 1 for the helium isoelectronic sequence fail to provide an adequate estimate of the correlation energy. Only BR provides the correct correlation energy for the helium atom, because it had been calibrated to do so. Wigner's is the only 0OA-type functional providing a mild dependence on the nuclear charge (Z), that mimics the exact correlation energy, though it is more than twice as large. In fact, the Wigner and BR correlation-energy functionals are the only local density functionals considered, that yield finite correlation energies for $Z \to \infty$. Needless to say, since PW is the definitive LDA limit, its failings should be taken as a genuine assessment of this level of approximation. That other 0OA-type correlation energies are in closer agreement with the exact results should be interpreted as fortuitous. It is regrettable that a "first-principles" benchmark 1OA correlation energy density cannot be specified in a similar way, or has not so far been proposed. For Hooke's atom all zero order approximations considered, presented in Fig. 5, are roughly equally poor. At intermediate values of the force constant the ordering

of the various approximations relative to the exact correlation energy is similar to that for the helium isoelectronic sequence.

The first-order functionals were split into two classes according to their behavior for the helium isoelectronic sequence. The more poorly behaved functionals, P86, OP and Becke, are presented in Fig. 2. They exhibit a strong dependence on the nuclear charge. The five functionals presented in Fig. 3 all have a reasonable slope, only mildly steeper than that of the exact correlation energy. Both PBE and Becke have been parameterized to yield the exact correlation energy for the helium atom. For Hooke's atom isoelectronic sequence most 1OA results, except P86, cluster together, being roughly twice as large as the exact correlation energy. We note that TPSS and FT97 are remarkably close to one another; so are PBE and PKZB. Neither pair remains close for the helium isoelectronic sequence. Rather, PBE and TPSS behave similarly; so do FT97 and PKZB, even more closely but further away from the exact correlation energy. These contradictory patterns serve as a warning against assigning excessive significance to limited scope examination of the comparative performance of different density functionals.

The three second-order approximations considered are presented, for the helium isoelectronic sequence, in Fig. 4. LYP has the overall most satisfactory behavior, although for $Z < 6$ CS is in closer agreement with the exact correlation energies. For Hooke's sequence (*cf.* Fig. 8), none of the second-order approximations provides a good agreement with the exact correlation energies. LYP and CS, which are conceptually related, are remarkably close to one another, along Hooke's atom isoelectronic sequence; however, this is not true for the helium isoelectronic sequence.

As already pointed out, Hooke's atom isoelectronic sequence allows the examination of the weak binding (high correlation) limit, $k \to 0$. The computed correlation energies for the range of lower force constants suggest that

$$\frac{E_c^{PW}}{E_c^{exact}} \approx 1 + 1.1 k^{\frac{1}{16}} ,$$

and

$$\frac{E_c^{GL}}{E_c^{exact}} \approx 1 + 2.18k^{\frac{1}{8}} ,$$

although, in both cases, the correlation energies are considerably higher than the exact correlation energies, even for the lowest force constants considered. These results may be taken to suggest that at very low force constants the local density approximation becomes exact, since the density is spread out and its gradient becomes negligibly low. A similar behavior is observed for the ratios $\frac{E_c^{FT97}}{E_c^{exact}}$, $\frac{E_c^{PKZB}}{E_c^{exact}}$ and $\frac{E_c^{TPSS}}{E_c^{exact}}$. This feature has not been deliberately built into any of these approximations. It is, therefore, noteworthy that it holds to the extent that it does.

Our study clearly suggests that the approximate density functionals in general perform better for the helium sequence than for Hooke's atoms. In order to understand this behavior we show in Fig. 9 scaled electron densities, i.e., ρ/c^3, as well as $\frac{d\rho}{dr}/c^4$ and $\frac{d^2\rho}{dr^2}/c^5$, as functions of $x = c \cdot r$ with c being $Z - 5/16$ for the He sequence and $k^{1/4} - 0.06649$ for Hooke's atoms. These scaling parameters were derived at the bottom of section 2, above.

A number of observations can be made from the figure. First, the curves for the He sequence are all remarkably similar, except for the region $r \to 0$, where the cusp problem becomes visible, in particular for the second-order derivative. An analogous similarity is not found for Hooke's atoms. The curves corresponding to the highest values of k are indeed very close to the expected $k \to \infty$ limit, but the range of k is broad enough to allow significant deviations from this limiting behavior. It follows that the He sequence does not provide a useful testing ground for exploring approximate density functionals, as long as it is not extended with further test systems.

Second, the electron density is more confined in space for the He sequence than for Hooke's atoms. For the former, the cusp problem may be important since the region for $r \to 0$ is one of a large energy density although its volume is vanishing. A similar region does not exist for Hooke's atoms, i.e., for those systems the electron density is not maximized in a region of diverging potential. This suggests a further reason for using Hooke's atoms as model systems for studying properties of electron densities in regions where the potential

stays finite. This is exactly what is relevant when developing approximate density functionals aimed at describing the properties of chemical bonds.

7 Conclusions

A word is appropriate about the choice of density functionals investigated. We did try to be fairly exhaustive. Some functionals were included primarily to respect the pioneers, most notably Wigner, although we have not made justice to contributions by Pines [50], Gell-Mann and Brueckner [51], Hedin [52], and many others. We did exclude a couple of recent functionals either because the correlation energies they provide for helium were judged to be poor, because no result was available to verify our implementation, or because they were considerably harder to implement. In the cases excluded we did not have a compelling reason to expect a particularly good performance for the helium sequence, let alone Hooke's sequence. We may have excluded highly worth-while functionals by oversight or ignorance, for which we apologize.

It has already been noted by several authors that most density functionals fail to yield an adequate dependence of the correlation energy on the nuclear charge, Z, along isoelectronic sequences. However, some, such as PBE, TPSS, CS and LYP are not too bad. None of that is true for Hooke's sequence, suggesting that the ultimate aim of developing a universal density functional has not yet been attained, not even for spherically-symmetric two-fermion systems. By analysing the electron densities for the two classes of systems, we found that the He sequence does not provide a sufficiently general class of systems for assessing or improving the quality of density functionals, whereas this is to a larger extent the case for Hooke's atom isoelectronic sequence. A feasible approach to improving the universality of correlation energy density functionals could be to examine their reparametrization, allowing for a dependence on the one-body potential. Since this potential is uniquely determined by the ground-state Hartree-Fock density, this approach is still consistent with the Hohenberg-Kohn framework of dft.

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Z	E_c^{exact}	E_c^{PW}	E_c^{GL}	E_c^{BR}	E_c^{W}
2	-0.042044	-0.1125[a]	-0.1385	-0.04204	-0.0959
3	-0.043498	-0.1346[b]	-0.1666	-0.05922	-0.1015
4	-0.044267	-0.1504[a]	-0.1862	-0.07276	-0.1043
5	-0.044736	-0.1628	-0.2037	-0.08376	-0.1059
6	-0.045054	-0.1730	-0.2137	-0.09290	-0.1071
7	-0.045281	-0.1817	-0.2240	-0.10065	-0.1079
8	-0.045452	-0.1893	-0.2330	-0.10730	-0.1085
9	-0.045586	-0.1960	-0.2409	-0.11309	-0.1090
10	-0.045692	-0.2020[a]	-0.2499	-0.11819	-0.1093
20		-0.2424	-0.2944	-0.14834	-0.1110
50		-0.2971	-0.3555	-0.17618	-0.1121

[a] ref. [12]. [b] ref. [53].

Table 1: Zero-order-approximation correlation energies for the Helium isoelectronic sequence. The approximate density functionals are defined in the text.

Z	E_c^{exact}	E_c^{PBE}	E_c^{PKZB}	E_c^{OP}	E_c^{FT97}	E_c^{TPSS}	E_c^{B88}	E_c^{P86}	E_c^{WL}
2	-0.042044	-0.04202[b]	-0.04727[b]	-0.05178[c]	-0.04623[d]	-0.04306[b]	-0.04189[e]	-0.04390[f]	-0.04204[a]
3	-0.043498	-0.04478[b]	-0.05063[b]	-0.06089	-0.04952	-0.04574[b]	-0.04985[e]	-0.04542[f]	-0.04418[e]
4	-0.044267	-0.04606[b]	-0.05224[b]	-0.06607	-0.05119	-0.04698[b]	-0.05462[e]	-0.04868[f]	-0.04520[e]
5	-0.044736	-0.04676	-0.05316	-0.06943	-0.05222	-0.04767	-0.05782	-0.05324	-0.04579
6	-0.045054	-0.04720	-0.05374	-0.07178	-0.05288	-0.04811	-0.06012	-0.05865	-0.04618
7	-0.045281	-0.04748	-0.05441	-0.07351	-0.05338	-0.04839	-0.06186	-0.06457	-0.04645
8	-0.045452	-0.04768	-0.05441	-0.07485	-0.05375	-0.04860	-0.06322	-0.07079	-0.04665
9	-0.045586	-0.04782	-0.05463	-0.07591	-0.05404	-0.04874	-0.06431	-0.07717	-0.04681
10	-0.045692	-0.04793	-0.05478	-0.07677	-0.05428	-0.04885	-0.06521	-0.08360	-0.04693[a]
20		-0.04826	-0.05536	-0.08080	-0.05535	-0.04923	-0.0695	-0.14274	-0.04749
50		-0.04824	-0.05550	-0.08335	-0.05602	-0.04928	-0.07240	-0.24874	-0.04781

[a] ref. [12]. [b] ref. [53]. [c] ref. [46]. [d] ref. [45]. [e] ref. [54]. [f] ref. [10].

Table 2: First-order-approximation correlation energies for the Helium isoelectronic sequence. The approximate density functionals are defined in the text.

Z	E_c^{exact}	E_c^{CS}	E_c^{LYP}	E_c^{FT98}
2	-0.042044	-0.04158[c]	-0.04378[a]	-0.04643[d]
3	-0.043498	-0.0439 [g]	-0.04755[e]	-0.05254
4	-0.044267	-0.04421[g]	-0.04905[a]	-0.05804
5	-0.044736	-0.04385	-0.04972	-0.06122
6	-0.045054	-0.04326	-0.05004	-0.06360
7	-0.045281	-0.04260	-0.05018	-0.06546
8	-0.045452	-0.04191	-0.05022	-0.06697
9	-0.045586	-0.04124	-0.05023	-0.06821
10	-0.045692	-0.04060	-0.05021[a]	-0.06925
20		-0.03591	-0.04992	-0.07464
50		-0.03001	-0.05008	-0.07862

[a] ref. [12]. [c] ref. [46]. [d] ref. [45] [e] ref. [54]. [g] ref. [4].

Table 3: Second-order-approximation correlation energies for the Helium isoelectronic sequence. The approximate density functionals are defined in the text.

k	E_c^{exact}	E_c^{PW}	E_c^{GL}	E_c^{BR}	E_c^{W}
0.000300891	-0.01691	-0.02865	-0.0303	-0.00392	-0.0388
0.00133497	-0.02198	-0.03857	-0.0425	-0.00609	-0.0506
0.01	-0.02904	-0.05478[h]	-0.0633	-0.01071	-0.0665
0.25	-0.03843	-0.08614[i]	-0.1045	-0.02424	-0.0871
1.0	-0.04134	-0.1013 [h]	-0.1243	-0.03321	-0.0935
16.	-0.04527	-0.1342	-0.1663	-0.05784	-0.1023
100.	-0.04684	-0.1575 [h]	-0.1952	-0.07847	-0.1060
10000.	-0.04877	-0.2208 [h]	-0.2699	-0.13417	-0.1105

[h] ref. [32]. [i] ref. [27]

Table 4: Zero-order-approximation correlation energies for Hooke's atom isoelectronic sequence. The approximate density functionals are defined in the text.

k	E_c^{exact}	E_c^{PBE}	E_c^{PKZB}	E_c^{OP}	E_c^{FT97}	E_c^{TPSS}	E_c^{B88}	E_c^{P86}	E_c^{WL}
0.000300891	-0.01691	-0.02148	-0.01895	-0.00970	-0.01904	-0.01835	-0.00860	-0.02508	-0.0385
0.00133497	-0.02198	-0.02782	-0.02525	-0.01446	-0.02483	-0.02416	-0.01247	-0.03244	-0.0475
0.01	-0.02904	-0.03705	-0.03470	-0.02341	-0.03292	-0.03260	-0.01951	-0.04216	-0.0577
0.25	-0.03843	-0.05118[j]	-0.04968	-0.04265	-0.04484	-0.04523	-0.03448	-0.05434	-0.0684
1.0	-0.04134	-0.05748	-0.05546	-0.05159	-0.04924	-0.04981	-0.04168	-0.05833	-0.0712
16.	-0.04527	-0.06520	-0.06522	-0.06768	-0.05652	-0.05708	-0.05547	-0.06712	-0.0746
100.	-0.04684	-0.06960	-0.07028	-0.07594	-0.06023	-0.06057	-0.06315	-0.07683	-0.0759
10000.	-0.04877	-0.07659[k]	-0.07861	-0.08816	-0.06624	-0.06569	-0.07563	-0.12609	-0.0774

[j] ref. [28]. [k] ref. [29].

Table 5: First-order-approximation correlation energies for Hooke's atom isoelectronic sequence. The approximate density functionals are defined in the text.

k	E_c^{exact}	E_c^{CS}	E_c^{LYP}	E_c^{FT98}
0.000300891	-0.01691	-0.01068	-0.01069	-0.01141
0.00133497	-0.02198	-0.01559	-0.01561	-0.01563
0.01	-0.02904	-0.02367	-0.02369	-0.02239
0.25	-0.03843	-0.03542	-0.03502[m]	-0.03488
1.0	-0.04134	-0.03837	-0.03762	-0.04057
16.	-0.04527	-0.03913	-0.03799	-0.05183
100.	-0.04684	-0.03636	-0.03573	-0.05879
10000.	-0.04877	-0.02397	-0.02871[m]	-0.07296

[m] ref. [55].

Table 6: Second-order-approximation correlation energies for Hooke's atom isoelectronic sequence. The approximate density functionals are defined in the text.

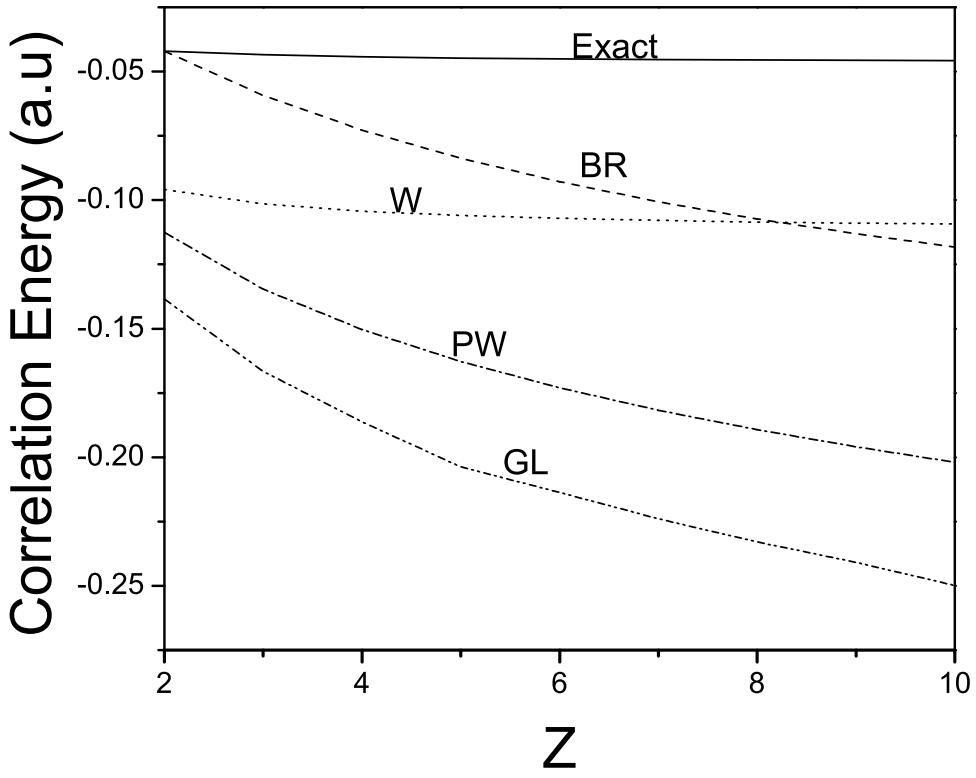

Figure 1: Zero-order-approximation correlation energies for the helium isoelectronic sequence. The approximate density functionals are defined in the text.

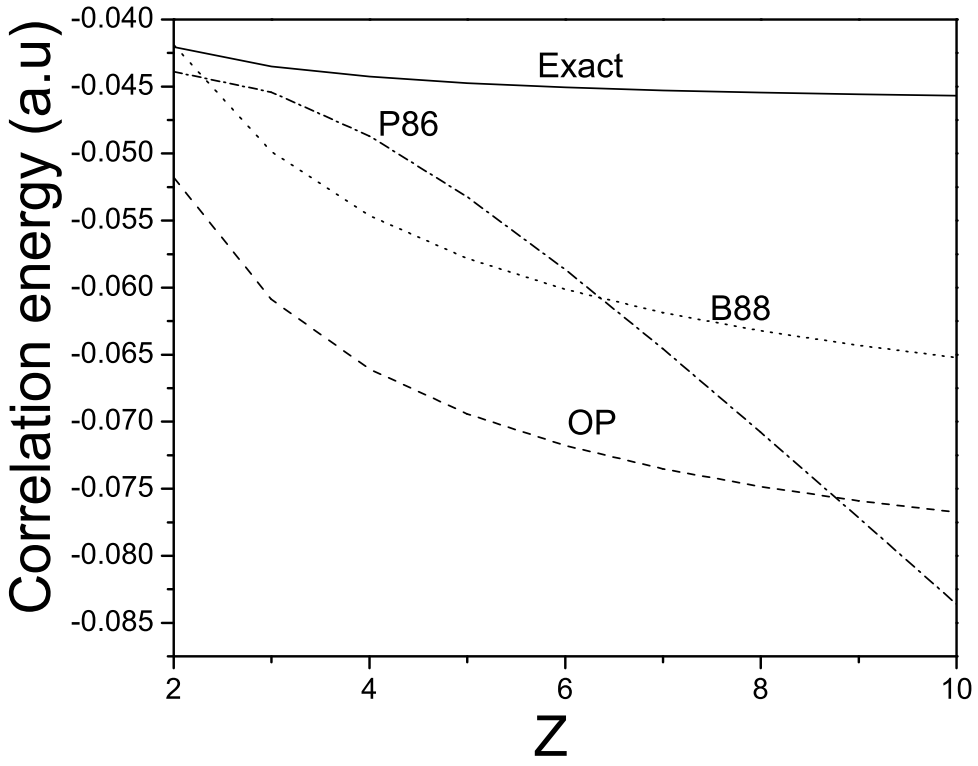

Figure 2: First-order-approximation correlation energies for the helium isoelectronic sequence for less-well performing functionals. The approximate density functionals are defined in the text.

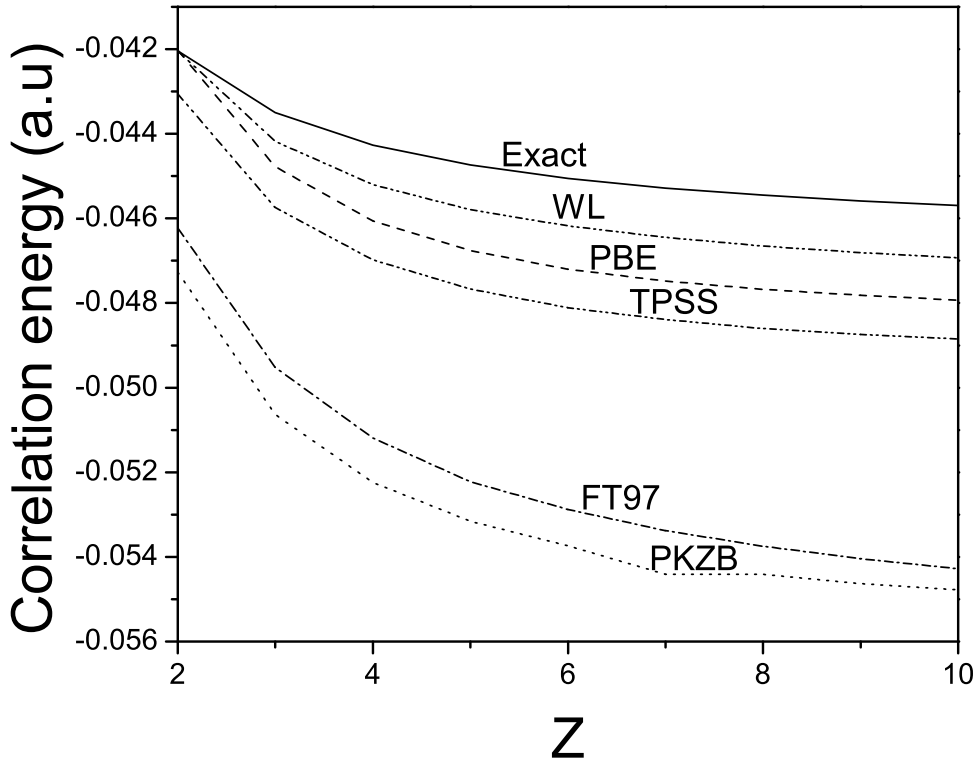

Figure 3: First-order-approximation correlation energies for the helium isoelectronic sequence for well performing functionals. The approximate density functionals are defined in the text.

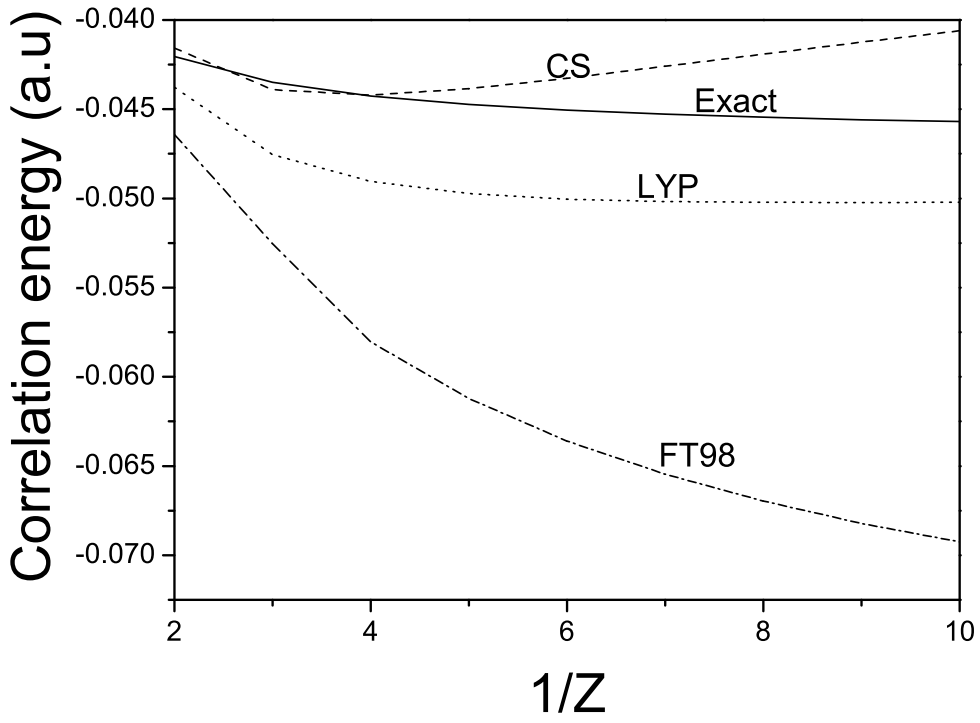

Figure 4: Second-order-approximation correlation energies for the helium isoelectronic sequence. The approximate density functionals are defined in the text.

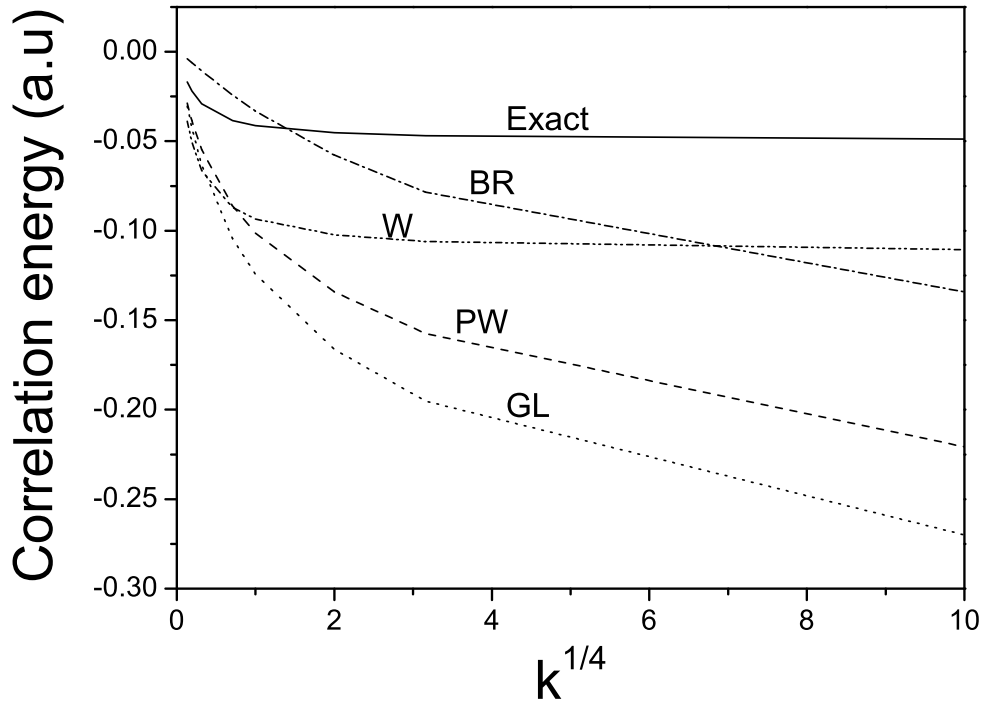

Figure 5: Zero-order-approximation correlation energies for Hooke's isoelectronic sequence. The approximate density functionals are defined in the text.

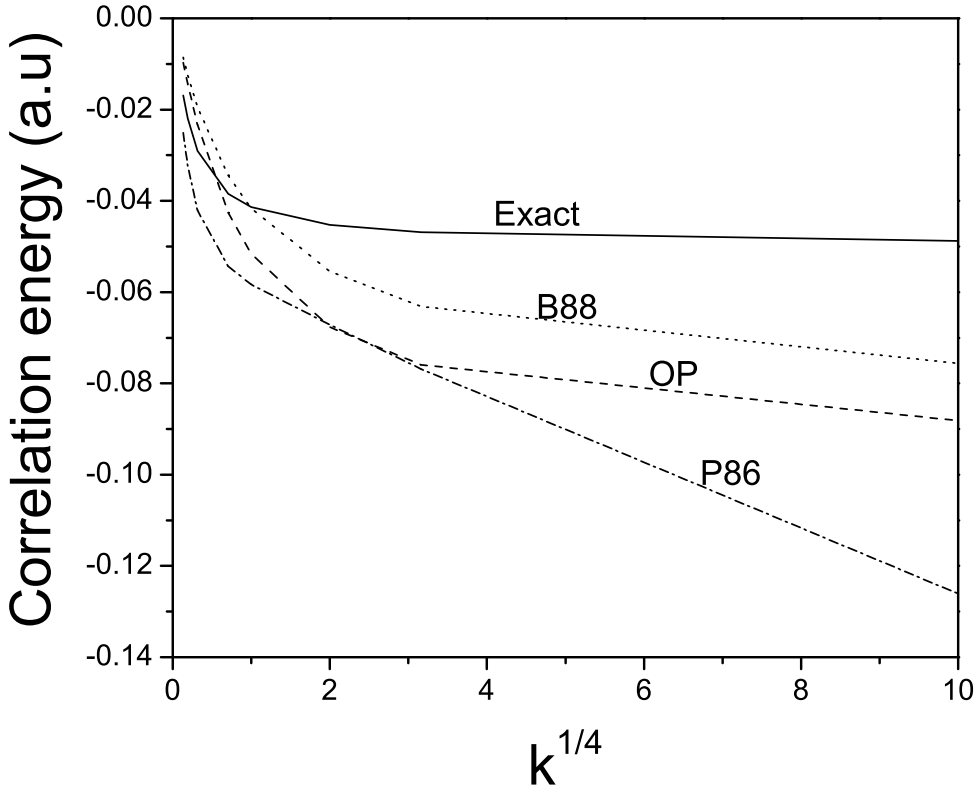

Figure 6: First-order-approximation correlation energies for Hooke's isoelectronic sequence for less-well performing functionals. The approximate density functionals are defined in the text.

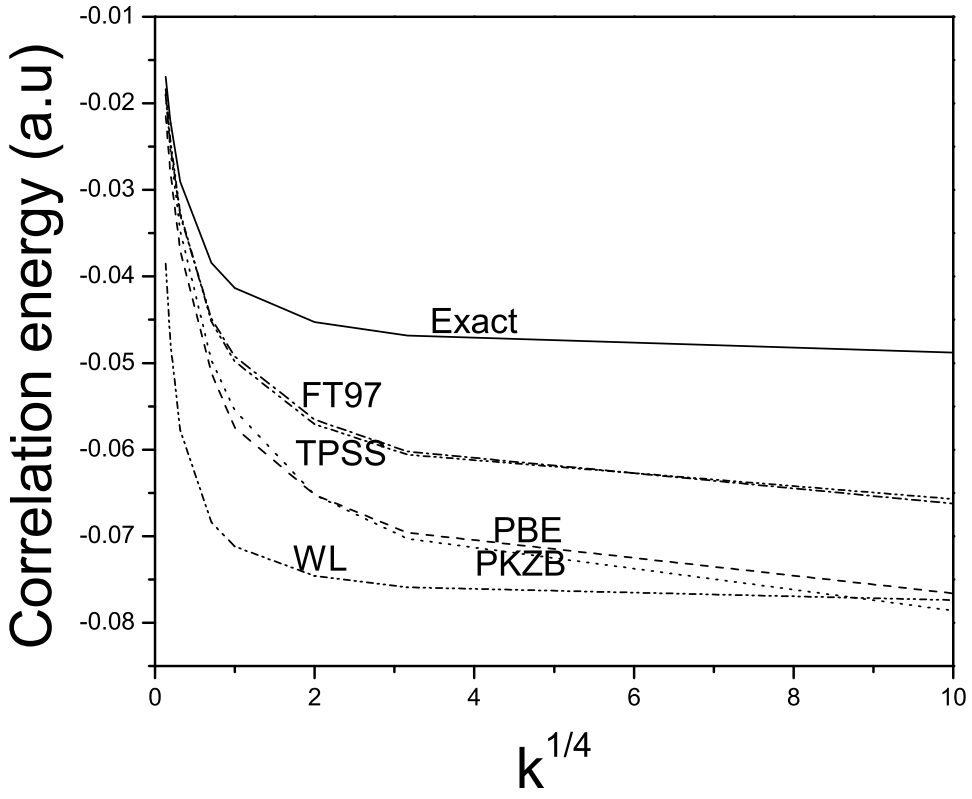

Figure 7: First-order-approximation correlation energies for Hooke's isoelectronic sequence for well performing functionals. The approximate density functionals are defined in the text.

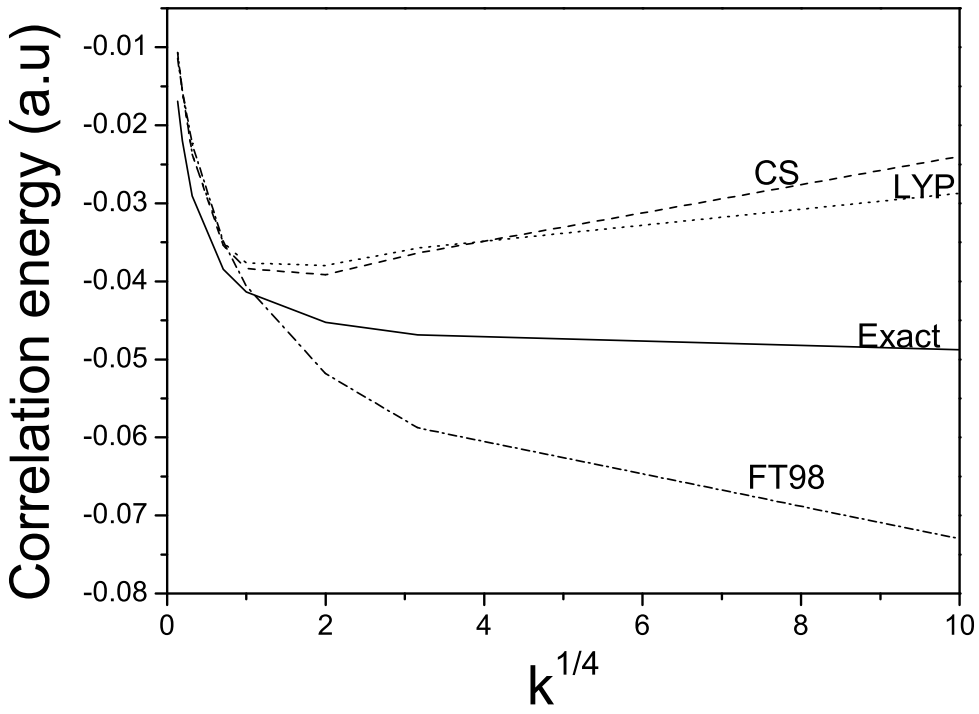

Figure 8: Second-order-approximation correlation energies for Hooke's isoelectronic sequence. The approximate density functionals are defined in the text.

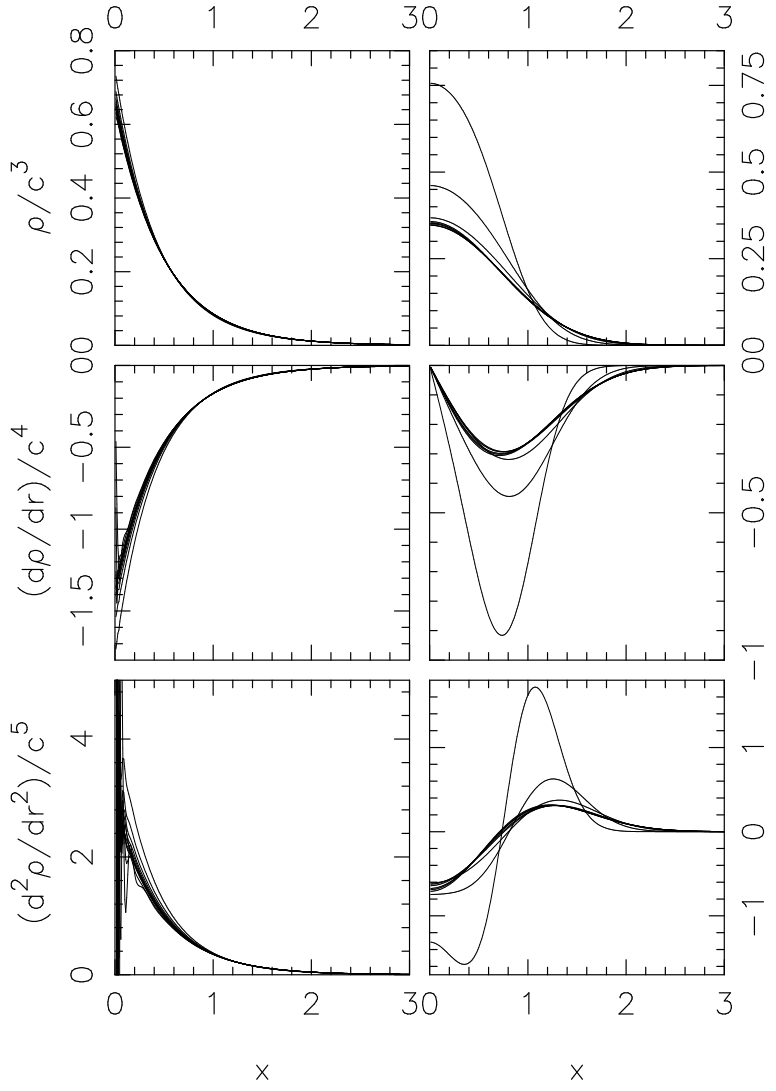

Figure 9: The electron density and its derivatives for the helium isoelectronic sequence (left panels) and Hooke's atom isoelectronic sequence (right panels). All curves are given as functions of a scaled radial coordinate $x = c \cdot r$, with c being $Z - 5/16$ for the He sequence and $k^{1/4} - 0.06649$ for Hooke's atoms. For Hooke's atoms, the uppermost curves for small x in the upper panel and the lowest curves for small x in the other two panels correspond to the largest values of k.